

EXHAUST GAS PURIFYING APPARATUS

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Abstract

PROBLEM TO BE SOLVED: To provide an exhaust gas purifying apparatus by which particulate (PM) and nitrogen oxides (NOx) in an exhaust gas is removed at a high NOx removal rate while evading sulfur poisoning that is a weak point of NOx storage reduction type catalyst.

SOLUTION: In the exhaust gas purifying apparatus provided with a wall flow type filter 4 provided in an exhaust passage 3 of an engine 2 and for purifying the particulate in the exhaust gas G, an oxidation catalytic layer 20 supporting an oxidation catalyst 21 is provided on the upstream part of a porous wall surface 30 of the filter 4 and a nitrogen oxide purifying catalyst layer 40 supporting the nitrogen oxide storage reduction type catalyst 41 containing a nitrogen oxide storage material 41a and an oxidation catalyst 41b is provided on the downstream side part of the porous wall surface 30 of the filter 4.

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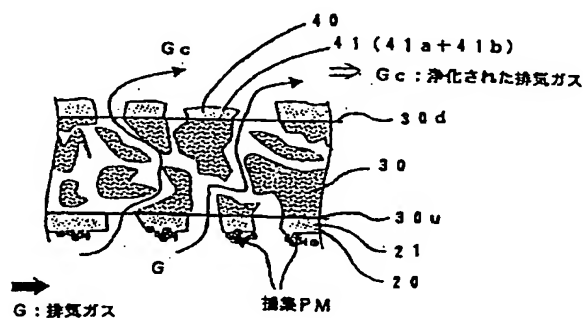
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(54) 【発明の名称】 排気ガス浄化装置

(57) 【要約】

【課題】 NO_x吸蔵還元型触媒の弱点である硫黄被毒を回避しながら、高いNO_x浄化率で、排気ガス中のP MとNO_xの浄化を行うことができる排気ガス浄化装置を提供する。

【解決手段】 エンジン2の排気通路3に設けられ、排気ガスG中の粒子状物質を浄化するウオールフロータイプのフィルタ4を備えた排気ガス浄化装置1において、前記フィルタ4の多孔質壁面30の上流側部分に酸化触媒21を担持した酸化触媒層20を設けると共に、前記フィルタ4の多孔質壁面30の下流側部分に窒素酸化物吸蔵物質41aと酸化触媒41bを含む窒素酸化物吸蔵還元型触媒41を担持した窒素酸化物浄化触媒層40を設ける。



【特許請求の範囲】

【請求項1】 エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化するウオールフロータイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの多孔質壁面の上流側部分に酸化触媒を担持した酸化触媒層を設けると共に、前記フィルタの多孔質壁面の下流側部分に窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を設けたことを特徴とする排気ガス浄化装置。

【請求項2】 エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化する繊維積層タイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの上流側の繊維層に酸化触媒を担持させるか又は酸化触媒を担持した酸化触媒層を積層すると共に、前記フィルタの下流側の繊維層に、窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持させるか又は該窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を積層したことを特徴とする排気ガス浄化装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、ディーゼルエンジン等の排気ガス中の粒子状物質及び窒素酸化物を、ディーゼルパティキュレートフィルタとこのフィルタに担持した窒素酸化物吸蔵還元型触媒で浄化する排気ガス浄化装置に関するものである。

【0002】

【従来の技術】ディーゼルエンジンから排出される粒子状物質（PM：パティキュレート：以下PM）の排出量は、窒素酸化物（以下NOx）、一酸化炭素（以下CO）そして炭化水素（以下HC）等と共に年々規制が強化され、エンジンの改良のみでは、これらの規制に対応しきれなくなっており、これらの物質を排ガス後処理装置によって、低減する技術が開発されている。

【0003】PMの捕集に関しては、ディーゼルパティキュレートフィルタ（DPF：Diesel Particulate Filter：以下DPF）があり、このPMを捕集するDPFには多孔質のコーディエライトやセラミック製のモノリスハニカムのウオールフロータイプのフィルタや、セラミックや金属を繊維状にしてランダムに積層した繊維積層タイプのフィルタ等が研究開発され提案されている。

【0004】このPM捕集用のDPFは、PMの捕集に伴って目詰まりが進行し、捕集したPMの量の増加に伴って排気ガス圧力（排圧）が上昇するので、捕集したPMを除去する必要があるが、最近では、PMの酸化除去を促進する酸化触媒をウオールフロータイプのフィルタの壁表面上に塗布した触媒付きフィルタで、PMの捕集と捕集したPMの酸化除去を連続的に行う連続再生型ディーゼルパティキュレートフィルタが提案されている。

【0005】このフィルタに担持させる酸化触媒には、排気ガス中の一酸化窒素（NO）を酸化して二酸化窒素

（NO₂）にする触媒や、PMを低温から直接酸素（O₂）で酸化させるPM酸化触媒（貴金属酸化触媒や酸化触媒）等がある。

【0006】一方、NOxの浄化に関しては、その一つの手段としてNOx還元触媒があり、特開2000-282852号公報では、ウオールフロータイプのフィルタの壁面のエンジン側にNOx還元触媒層と酸化触媒層を被覆した排気浄化装置と、ウオールフロータイプのフィルタの壁面のエンジン側に酸化触媒を、排気出口側にNOx還元触媒層をそれぞれ被覆した排気浄化装置が提案されている。

【0007】これらの排気浄化装置では、フィルタと貴金属系触媒等の酸化触媒層とゼオライト系触媒等のNOx還元触媒層を一体化して装置を小型軽量化すると共に、酸化触媒層とNOx還元触媒層の配置の工夫により、酸化触媒でPMの燃焼の促進して、NOx還元触媒へのPM付着によるNOx還元効率の低下を回避し、また、フィルタ再生時のPM燃焼時のNOx還元触媒への熱影響を少なくしてNOx還元触媒の劣化を防止している。

【0008】

【発明が解決しようとする課題】しかしながら、特開2000-282852号公報で提案されている、これらの排気浄化装置においては、NOx浄化に、NOx還元触媒を使用しているので、NOx還元のために常時炭化水素等の還元剤を供給する必要があり、この還元剤を供給するための還元剤供給装置が必要となる。

【0009】そして、この還元剤にエンジンの燃料を流用した場合には、燃料を排気通路に噴射するための噴射弁や配管が必要になる上に、燃費の悪化を招くという問題があり、また、エンジンの燃料以外のアンモニアや尿素を使用する場合には、噴射弁や配管に加えて、これらの還元剤用のタンクが必要になる上に、これらの還元剤を還元剤用のタンクに適宜補給する必要があるという問題がある。

【0010】この排気通路への還元剤供給システムの設置が必要になると、特に既存の車両に、排気ガス装置を取り付ける際の作業が面倒になるので、装置面からも作業工数の面からコストアップとなり実用化が難しくなるという問題が発生する。

【0011】また、特に、還元剤を必要とするNOx還元触媒の上流側に酸化触媒が配置されているため、還元剤が軽油の場合には酸化触媒により分解されてNOx還元効率のよい低分子量の炭化水素になり、また、SOF（可溶性有機成分）も分解されて還元剤として、効率よくNOxを還元するとされているが、ディーゼルエンジンの通常の燃焼状態のように排気中の酸素濃度が高い場合には、排気通路内に供給された還元剤は、上流側の酸化触媒によって酸化される可能性が大きく、NOx還元効率も低下し、燃費の悪化を招くと考えられる。

【0012】一方、排気ガス中の NO_x を除去するための触媒の一つに、 NO_x 吸蔵還元型触媒がある。この NO_x 吸蔵還元型触媒は、 NO_x 吸蔵機能を持つバリウム等の NO_x 吸蔵物質と酸化触媒機能を有する白金等の活性触媒金属（酸化触媒）とを担持して、排気ガス中の酸素濃度等によって NO_x 吸蔵と NO_x 放出及び還元浄化の機能を果たす触媒である。

【0013】本発明は、上述の問題を解決するためになされたものであり、その目的は、DPFのフィルタの上流側部分に酸化触媒を、また、下流側部分に NO_x 吸蔵還元型触媒をそれぞれ配備し、 NO_x 吸蔵還元型触媒の弱点である硫黄被毒を回避しながら、高い NO_x 浄化率で、排気ガス中のPMと NO_x の浄化を行うことができる排気ガス浄化装置を提供することにある。

【0014】

【課題を解決するための手段】以上のような目的を達成するための排気ガス浄化装置は、次のように構成される。

【0015】1) エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化するウオールフロータイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの多孔質壁面の上流側部分に酸化触媒を担持した酸化触媒層を設けると共に、前記フィルタの多孔質壁面の下流側部分に窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を設けて構成される。

【0016】このウオールフロータイプのフィルタは、多孔質のセラミックのハニカムのチャンネルの入口と出口を交互に目封じたモノリスハニカム等で形成でき、酸化触媒を担持した酸化触媒層は、このフィルタの多孔質壁面に塗布されたゼオライトやアルミナ等の多孔質触媒コート層に、白金(Pt)や酸化セリウム(CeO_2)等の酸化触媒を担持する等して形成できる。

【0017】また、窒素酸化物(NO_x)吸蔵還元型触媒は、排気ガス中の O_2 濃度やCO濃度によって NO_x 吸蔵と NO_x 放出及び還元・浄化の機能を持つものであり、 NO_x 吸蔵機能を持つカリウム(K)、バリウム(Ba)、ランタン(La)等の NO_x 吸蔵物質と、白金(Pt)やロジウム(Rh)等の触媒活性金属からなる酸化触媒とで形成でき、 NO_x 浄化触媒層は、フィルタの多孔質壁面に塗布されたゼオライトやアルミナ等の多孔質触媒コート層に、これらの NO_x 吸蔵物質と酸化触媒を担持する等して形成できる。

【0018】2) または、エンジンの排気通路に設けられ、排気ガス中の粒子状物質を浄化する繊維積層タイプのフィルタを備えた排気ガス浄化装置において、前記フィルタの上流側の繊維層に酸化触媒を担持させるか又は酸化触媒を担持した酸化触媒層を積層すると共に、前記フィルタの下流側の繊維層に、窒素酸化物吸蔵物質と酸化触媒を含む窒素酸化物吸蔵還元型触媒を担持させるか

又は該窒素酸化物吸蔵還元型触媒を担持した窒素酸化物浄化触媒層を積層して構成される。

【0019】この繊維積層タイプのフィルタには、アルミナ等のセラミックの繊維や金属繊維をランダムに積層した不織布の繊維層を一層乃至数層重ねて形成し、この繊維層の積層体を耐熱金網で挟持し蛇腹状に折り曲げて中空円筒状に構成して、外側から内側へ排気ガスを流通させることにより、排気ガスを浄化するフィルタ等がある。

【0020】この上流側又は下流側の繊維層をそれぞれの触媒の溶液に浸せきして、繊維層を形成する繊維表面にそれぞれの触媒を担持させて形成する。又は、繊維積層タイプのフィルタの繊維層の積層体の上流側の繊維層の表面に酸化触媒を担持した多孔質触媒コート層を塗布し、また、下流側の繊維層の表面に上記と同様な NO_x 吸蔵還元型触媒を担持した多孔質触媒コート層を塗布する。

【0021】これらの構成により、フィルタの上流側部分に酸化触媒を、また、下流側に NO_x 吸蔵還元型触媒をそれぞれ担持させることにより、上流側の酸化触媒で排気ガス中の硫黄酸化物(SO_x)を酸化し、排気ガス中のCa、Zn、Fe等と化合させて、固体のサルフェートにして、フィルタに捕集させるので、 SO_x の NO_x 吸蔵還元型触媒への到達を防止でき、 NO_x 吸蔵還元型触媒の硫黄被毒を回避できる。

【0022】そして、 NO_x 吸蔵還元型触媒は、一酸化炭素(CO)が存在すると、 NO_x 吸蔵物質から二酸化窒素(NO_2)を放出する特性を持っているために、空燃比がリーンの NO_x 吸蔵運転の時に、排気ガス中にCOが存在すると、 NO_x 吸蔵能力が低下してしまうが、本発明の排気ガス浄化装置では、上流側の酸化触媒で排気ガス中のCOを酸化して除去するので、空燃比がリーン時における NO_x 吸蔵能力を高く維持できる。

【0023】また、空燃比がリッチの再生運転の時には、排気ガス中に酸素(O_2)が無いために、大量のCOが発生するので、このCOが NO_x 吸蔵物質からの NO_2 の放出を促進すると共に、このCOは還元剤となるので、放出された NO_2 は NO_x 吸蔵還元型触媒の酸化触媒により効率よく還元浄化される。

【0024】

【発明の実施の形態】以下、本発明に係る実施の形態の排気ガス浄化装置について、図面を参照しながら説明する。

【0025】図1に、この第1の実施の形態の排気ガス浄化装置1の構成を示す。

【0026】この排気ガス浄化装置1は、図1に示すように、ディーゼルエンジン2の排気通路3に設けられる装置であり、排気ガスG中の粒子状物質(PM)と窒素酸化物(NO_x)を浄化するウオールフロータイプのフィルタ4を備えて構成される。

【0027】図2に示すように、このウォールフロータイプのフィルタ4は、コーディエライト、炭化ケイ素(SiC)やステンレス等で形成される構造材の担持体30に、排気ガスGの通路となる多数の多角形状のチャンネル(セル)35を有しており、多孔質のセラミックのハニカムのチャンネル35の入口と出口を交互に目封じたモノリスハニカム等で形成される。

【0028】そして、図3及び図4に示すように、このフィルタ4の多孔質壁面30の上流側部分30uに、酸化触媒21を担持した通気可能な酸化触媒層20を設けると共に、フィルタ4の多孔質壁面30の下流側部分30dに、窒素酸化物吸蔵物質(NO_x吸蔵物質)41aと酸化触媒41bを含む窒素酸化物吸蔵還元型触媒(NO_x吸蔵還元型触媒)41を担持した通気可能なNO_x浄化触媒層40を設ける。

【0029】この酸化触媒層20は、このフィルタ4の多孔質壁面30の上流側部分30uに塗布されたゼオライトやアルミナ(A₁, O₂)等の多孔質触媒コート層に、白金(Pt)等や酸化セリウム(CeO₂)等の酸化触媒21を担持して通気可能に形成される。

【0030】また、NO_x浄化触媒層40は、フィルタ2の多孔質壁面30の下流側部分30dに塗布されたゼオライトやアルミナ等の多孔質触媒コート層に、NO_x吸蔵物質41aと酸化触媒41bとからなるNO_x吸蔵還元型触媒41を担持して形成される。

【0031】このNO_x吸蔵物質41aはNO_x吸蔵機能を持つカリウム(K)、バリウム(Ba)、ナトリウム(Na)、リチウム(Li)、セシウム(Cs)等のアルカリ金属や、カルシウム(Ca)等のアルカリ土類、ランタン(La)、イットリウム(Y)等の希土類等の一つ又は幾つかの組み合わせで形成され、酸化触媒41bは白金(Pt)やロジウム(Rh)等の触媒活性金属で形成される。

【0032】この構成により、NO_x吸蔵還元型触媒41は、図9に模式的に示すように、排気ガス中の空燃比がリーン状態(O₂濃度が比較的高い)の時にNO_x吸蔵物質41bでNO_xを吸蔵し、空燃比がリッチ状態(O₂濃度が殆どゼロ)の時にNO_x吸蔵物質41bでNO_xを放出し、この放出したNO_xを、酸化触媒41bの触媒作用によりCOやHC等の還元剤で還元して浄化する機能を持つことになる。

【0033】次に、第2の実施の形態の排気ガス浄化装置1Aについて説明する。

【0034】この第2の実施の形態の排気ガス浄化装置1Aは、図5～図7に示すように、第1の実施の形態の排気ガス浄化装置1と排気ガス中の粒子状物質(PM)を浄化するフィルタのタイプが異なる。

【0035】この第2の実施の形態のフィルタ4A、4B、4Cは、図5～図10に示すように、繊維積層タイプのフィルタで形成され、アルミナ等のセラミックの繊

維や金属繊維をランダムに積層した不織布の繊維層5a～5dを一層乃至数層重ねて形成し、この繊維層5a～5dの積層体5A、5B、5Cを耐熱金網6、7で挟持し蛇腹状に折り曲げて中空円筒状に構成し、この中空円筒の一端側4aを閉塞する。排気ガスGは、この中空円筒状の繊維層5a～5dの積層体5A、5B、5Cの外側から内側へ流通し浄化され、中空部4bの他端側4cから外部へ排出される。

【0036】そして、図8及び図9に示すように、このフィルタ4A、4Bの上流側の繊維層5aの表面に、酸化触媒21を担持した多孔質触媒コート層20を塗布し、また、下流側の繊維層5dの表面にNO_x吸蔵還元型触媒41を担持した多孔質触媒コート層40を塗布する。図8は、繊維層5aの耐熱金網6側、及び繊維層5dの耐熱金網7側に、多孔質触媒コート層20、40を設けた積層体5Aの例を示し、図9は、繊維層5aと繊維層5bとの間、及び繊維層5dと繊維層5cとの間に、多孔質触媒コート層20、40を設けた積層体5Bの例を示す。

【0037】若しくは、上流側又は下流側の繊維層5a、5dをそれぞれの触媒31、41の溶液に浸せきした後乾燥及び熱処理して繊維層5a、5dを形成する繊維表面にそれぞれの触媒31、41を担持させてから、図10に示すように、この触媒31、41を担持した繊維層5a'、5d'を、触媒を担持していない繊維層5b、5cに積層して、積層体5Cを形成する。なお、フィルタ4Cを構成する繊維層5a～5d全部にいずれかの触媒を担持させて、触媒を担持していない繊維層を省いて形成してもよい。

【0038】以上の構成の排気ガス浄化装置1、1Aによれば、排気ガスGは酸化触媒21に接触し他後に、フィルタ4、4A～4Cを通過して、更に、NO_x吸蔵還元型触媒41に接触してから排出されるので、次のようなプロセスで効率よく浄化される。

【0039】先ず、通常のディーゼルエンジンや希薄燃焼ガソリンエンジン等の通常運転のように、排気ガス中にO₂が含まれる空燃比がリーンの酸素濃度が比較的高い状態では、図11に示すように、フィルタ4、4A～4Cの上流側の酸化触媒21や下流側のNO_x吸蔵還元型触媒の酸化触媒41bで、排気ガスG中のNOは、この排気ガスG中のO₂により酸化されてNO₂になり、このNO₂は、バリウム(Ba)等のNO_x吸蔵物質41aが硝酸塩(例えばBa(NO₃)₂)等の形で吸蔵するので、排気ガスG中のNO_xが浄化される。

【0040】また、上流側の酸化触媒21で、排気ガスG中のHC、COを酸化浄化し、NO_x吸蔵還元型触媒41のCOによるNO_x吸蔵能力の劣化を防止する。また、SOOT(スート：煤)等のPMはフィルタ4、4A～4Cの多孔質壁面30や繊維の積層体5A～5Cで捕集される。

【0041】しかし、この状態が継続すると、NO_x吸蔵機能を持つNO_x吸蔵物質41aは、全て硝酸塩等に変化してNO_x吸蔵機能を失ってしまうので、エンジンの運転状態を変更して、理論空燃比及び理論空燃比に近い空燃比であるリッチ燃焼を短時間（例えば、約0.1秒～5秒程度）の間だけ行って、リッチスパイクガスと呼ばれる、排気ガス中のO₂を略ゼロとした高温の排気ガスを発生させて、NO_x吸蔵還元型触媒41に送り、再生処理する。

【0042】そして、NO_x吸蔵還元型触媒41を再生する空燃比がリッチの酸素濃度は殆どゼロの状態では、フィルタ4、4A～4Cの上流側では、O₂が殆どないため、HC、COは酸化されることなく、下流側に通過し、下流側ではO₂が殆どないので、図12に示すように、NO_xを吸蔵したNO_x吸蔵物質41aの硝酸塩（硝酸バリウム）等は元の状態（バリウム）に戻り、吸蔵していたNO_xを放出する。

【0043】この再生時には、COが多いため、NO_x吸蔵物質41aからのNO_xの放出と還元浄化を促進させることができるので、NO_x吸蔵能力の再生に要する時間を短縮できる。

【0044】この放出されたNO_xは、排気ガス中にO₂が存在しないので、酸化触媒41bの触媒作用により多孔質壁面30や繊維の積層体5A～5Cを通過してきた排気ガス中のCO、HC、H₂等を還元剤として、窒素N₂に還元され浄化され、H₂O、CO₂と共に排出される。また、SOOT等のPMは多孔質壁面30や繊維の積層体5A～5Cで捕集される。

【0045】そして、排気ガス中の硫黄酸化物（SO_x）を上流側の酸化触媒31で酸化して、排気ガス中のCa、Zn、Fe等と化合させて、固体のサルフェートにすることができ、このサルフェートは多孔質壁面30や繊維の積層体5A～5Cで捕集できるので、SO_xのNO_x吸蔵還元型触媒41への接触を防止して、NO_x吸蔵還元型触媒41の硫黄被毒を回避できる。

【0046】

【発明の効果】以上に説明したように、本発明の排気ガス浄化装置によれば、次のような効果を奏することができる。

【0047】常時NO_x還元用の還元剤を供給することなく、酸化触媒とNO_x吸蔵還元型触媒を担持したフィルタにより、排気ガス中のPMを捕集及び酸化して浄化できると共に、排気ガス中のNO_xをNO_x吸蔵還元型触媒による吸蔵、及び放出と還元により、効率よく浄化することができるので、還元剤供給装置が不要になり、燃費の悪化を防止できる。

【0048】そして、フィルタの上流側部分に酸化触媒を、また、下流側部分にNO_x吸蔵還元型触媒を配設する構成により、上流側部分の酸化触媒で排気ガス中の硫黄酸化物（SO_x）を酸化して、排気ガス中のCa、Z

n、Fe等と化合させて、フィルタで捕集できる固体のサルフェートとし、フィルタで捕集するので、排気ガス中のSO_xがNO_x吸蔵還元型触媒への到達するのを防止でき、NO_x吸蔵還元型触媒の硫黄被毒を回避できる。

【0049】更に、空燃比がリッチのNO_x吸蔵運転において、フィルタの上流側の酸化触媒で排気ガス中のCOを酸化除去するので、COによるNO_x吸蔵能力の劣化を防止して高い浄化率を維持でき、また、空燃比がリッチの再生運転において、排気ガス中にO₂が無いために発生するCOで、NO_x吸蔵物質からのNO_xの放出と還元浄化を促進させることができ、NO_x吸蔵能力の再生に要する時間を短縮できる。

【図面の簡単な説明】

【図1】本発明に係る排気ガス浄化装置の配置を示す図である。

【図2】本発明に係る第1の実施の形態の排気ガス浄化装置のウォールフロータイプのフィルタの構成を示す図である。

【図3】図2のフィルタの拡大図である。

【図4】図2のフィルタの部分拡大図である。

【図5】本発明に係る第2の実施の形態の排気ガス浄化装置の繊維積層タイプのフィルタの構成を示す図である。

【図6】図5のフィルタにおける排気ガスの流れを示す図である。

【図7】図6の部分拡大図である。

【図8】図5のフィルタの積層構造の第1例を示す図である。

【図9】図5のフィルタの積層構造の第2例を示す図である。

【図10】図5のフィルタの積層構造の第3例を示す図である。

【図11】NO_x吸蔵還元型触媒によるNO_x浄化のメカニズムを示す模式的な図で、通常燃焼等の空燃比がリッチ状態の排気ガスを供給している状態を示す。

【図12】NO_x吸蔵還元型触媒によるNO_x排気浄化のメカニズムを示す模式的な図で、空燃比がリッチ状態の排気ガスを供給している状態を示す。

【符号の説明】

- 1、1A、1B、1C 排気ガス浄化装置
- 2 エンジン
- 3 排気通路
- 4 ウォールフロータイプのフィルタ
- 4A、4B、4C 繊維積層タイプのフィルタ
- 4a 上流側の繊維層
- 4d 下流側の繊維層
- 20 酸化触媒層（多孔質触媒コート層）
- 21 酸化触媒
- 30 多孔質壁面

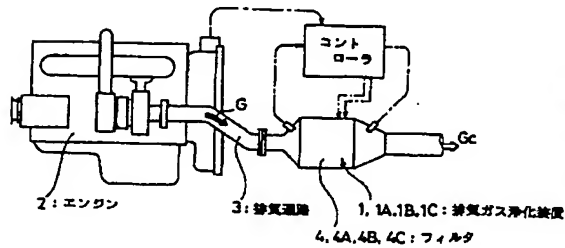
40 窒素酸化物浄化触媒層（多孔質触媒コート層）
 41 窒素酸化物吸蔵還元型触媒（NO_x吸蔵還元型触媒）

* 41a 窒素酸化物吸蔵物質（NO_x吸蔵物質）

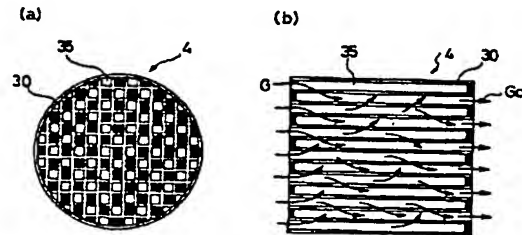
41b 酸化触媒

* G 排気ガス

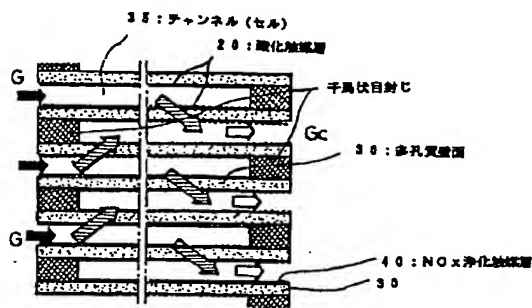
【図1】



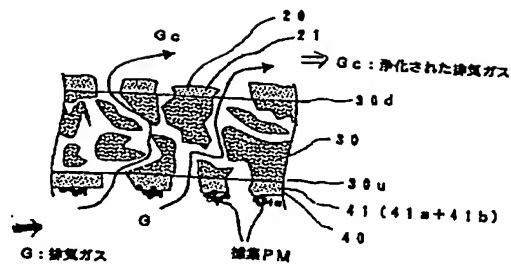
【図2】



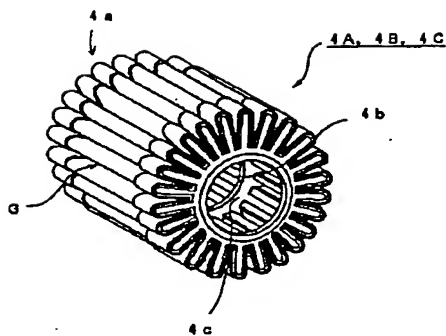
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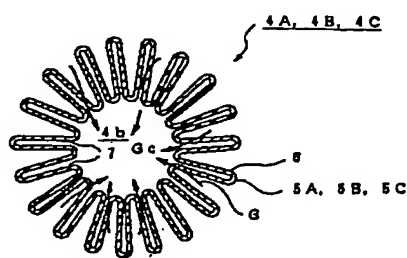
【図4】



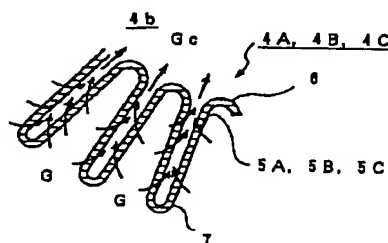
【図5】



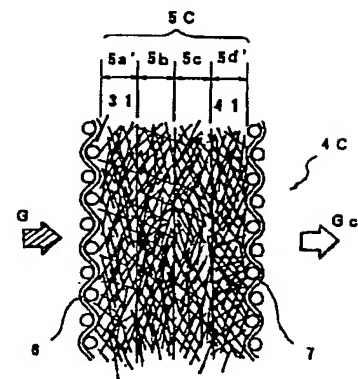
【図6】



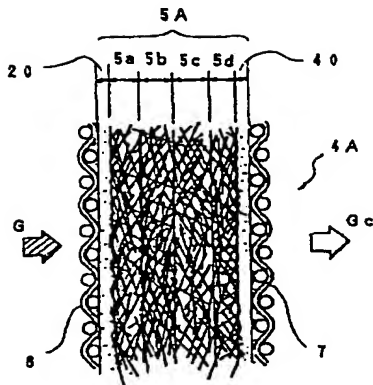
【図7】



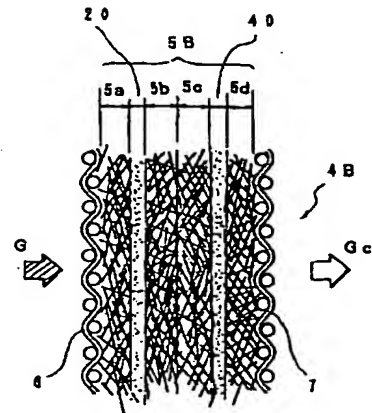
【図10】



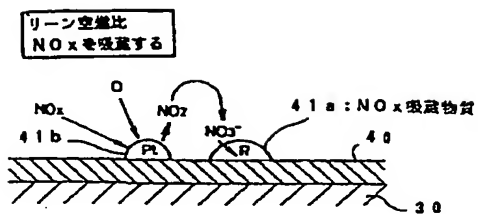
【図8】



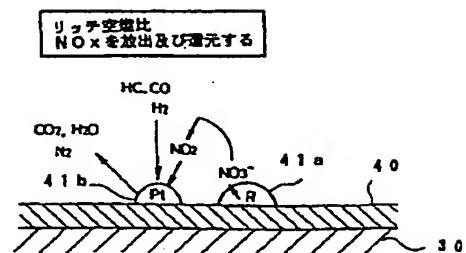
【図9】



【図11】



【図12】



【手続補正書】

【提出日】平成13年8月8日(2001. 8. 8)

*【補正方法】変更

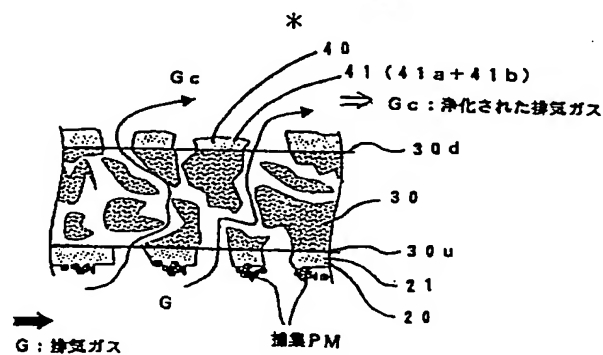
【手続補正1】

【補正内容】

【補正対象書類名】図面

【図4】

【補正対象項目名】図4



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	3/24			3/28	3 0 1 E
					3 0 1 P
	3/28	3 0 1	B 0 1 D	53/36	1 0 3 C
					1 0 3 B
					Z A B

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 GB05W GB06W GB09X GB10W
 GB17X HA15 HA16

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 CA01 CA02 CA03 CB04

4D048 AA06 AA14 AB01 AB02 AB07
 BA03X BA06X BA10X BA11X
 BA14X BA15X BA18X BA19X
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(71)Applicant : ISUZU MOTORS LTD

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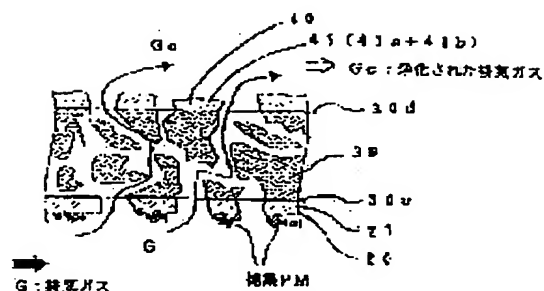
(72)Inventor : TASHIRO YOSHIHISA

(54) EXHAUST GAS PURIFYING APPARATUS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an exhaust gas purifying apparatus by which particulate (PM) and nitrogen oxides (NOx) in an exhaust gas is removed at a high NOx removal rate while evading sulfur poisoning that is a weak point of NOx storage reduction type catalyst.

SOLUTION: In the exhaust gas purifying apparatus provided with a wall flow type filter 4 provided in an exhaust passage 3 of an engine 2 and for purifying the particulate in the exhaust gas G, an oxidation catalytic layer 20 supporting an oxidation catalyst 21 is provided on the upstream part of a porous wall surface 30 of the filter 4 and a nitrogen oxide purifying catalyst layer 40 supporting the nitrogen oxide storage reduction type catalyst 41 containing a nitrogen oxide storage material 41a and an oxidation catalyst 41b is provided on the downstream side part of the porous wall surface 30 of the filter 4.



LEGAL STATUS

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18.02.2005

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[Date of final disposal for application]

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[Date of registration]

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CLAIMS

[Claim(s)]

[Claim 1] The exhaust gas purge characterized by preparing the nitrogen-oxides purification catalyst bed which supported the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occluded substance and an oxidation catalyst in the downstream part of the porosity wall surface of said filter while being prepared in the engine flueway and preparing the oxidation catalyst layer which supported the oxidation catalyst into the upstream part of the porosity wall surface of said filter in the exhaust gas purge equipped with the filter of the Wall flow type which purifies the particulate matter in exhaust gas.

[Claim 2] In the exhaust gas purge equipped with the filter of the fiber laminating type which is formed in an engine flueway and purifies the particulate matter in exhaust gas While carrying out the laminating of the oxidation catalyst layer which the fiber layer of the upstream of said filter was made to support an oxidation catalyst, or supported the oxidation catalyst The exhaust gas purge characterized by carrying out the laminating of the nitrogen-oxides purification catalyst bed which was made to support the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occluded substance and an oxidation catalyst in the fiber layer of the downstream of said filter, or supported this nitrogen-oxides occlusion reduction type catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the exhaust gas purge which purifies the particulate matter and nitrogen oxides in exhaust gas, such as a diesel power plant, with the nitrogen-oxides occlusion reduction type catalyst supported in a diesel particulate filter and this filter.

[0002]

[Description of the Prior Art] The technique of regulation being tightened up every year with nitrogen oxides (henceforth, NOx), a carbon monoxide (henceforth, CO), a hydrocarbon (henceforth, HC), etc., and it being impossible for the discharge of the particulate matter (PM; particulate: henceforth, PM) discharged from a diesel power plant to be unable to respond to these regulations only by engine amelioration, and reducing these matter with exhaust gas after-treatment equipment is developed.

[0003] About the uptake of PM, there is a diesel particulate filter (DPF: Diesel Particulate Filter: henceforth, DPF), and the Wall flow type filter of the monolith honeycomb of porous cordierite or the product made from a ceramic, the filter of the fiber laminating type which made the ceramic metallurgy group fibrous and carried out the laminating at random, etc. are done [research and development in them etc.] and proposed by DPF which carries out uptake of this PM.

[0004] Blinding advances in connection with the uptake of PM, and although DPF for these PM uptake needs to remove PM which carried out uptake since the exhaust-air-pressure force (exhaust gas pressure) goes up with the increment in the amount of PM which carried out uptake. Recently, the continuation playback mold diesel particulate filter which performs continuously oxidation removal of PM which carried out uptake to the uptake of PM is proposed with the filter with a catalyst which applied the oxidation catalyst which promotes oxidation removal of PM on the wall front face of a Wall flow type filter.

[0005] There are a catalyst which oxidizes and uses the nitrogen monoxide in exhaust gas (NO) as a nitrogen dioxide (NO2), a PM oxidation catalyst (a noble-metals oxidation catalyst and oxide oxidation catalyst) which oxidizes PM with direct oxygen (O2) from low temperature as oxidation catalyst which this filter is made to support.

[0006] On the other hand, about purification of NOx, there is an NOx reduction catalyst as the one means, and the exhaust emission control device which covered the NOx reduction catalyst layer, respectively is proposed by the exhaust air outlet side in the oxidation catalyst by JP.2000-282852.A at the engine side of the wall surface of the exhaust emission control device which covered the NOx reduction catalyst layer and the oxidation catalyst layer to the engine side of the wall surface of a Wall flow type filter, and a Wall flow type filter.

[0007] While unifying a filter, oxidation catalyst layers, such as a noble-metals system catalyst, and NOx reduction catalyst layers, such as a zeolitic catalyst, and forming equipment into small lightweight in these exhaust emission control devices. By the device of arrangement of an oxidation catalyst layer and an NOx reduction catalyst layer, combustion of PM promotes by the oxidation catalyst. Decline in the NOx reduction effectiveness by PM adhesion in an NOx reduction catalyst was avoided, and the thermal effect to the NOx reduction catalyst at the time

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.ejie

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JP.2003-001067.A [DETAILED DESCRIPTION]

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NOx occluded substances, such as a potassium (K) which has the function of NOx occlusion, NOx emission, and reduction and purification, and has an NOx occlusion function with concentration or CO concentration, barium (Ba), and a lanthanum (La). It can form by the oxidation catalyst which consists of catalytic activity metals, such as platinum (Pt) and a rhodium (Rh), and an NOx purification catalyst bed can be formed in porous catalyst coat layers applied to the porosity wall surface of a filter, such as a zeolite and an alumina, by carrying out supporting these NOx occluded substances and oxidation catalysts etc.

[0018] 2) Or it is prepared in an engine flueway and set to the exhaust gas purge equipped with the filter of the fiber laminating type which purifies the particulate matter in exhaust gas. While carrying out the laminating of the oxidation catalyst layer which the fiber layer of the upstream of said filter was made to support an oxidation catalyst, or supported the oxidation catalyst. The laminating of the nitrogen-oxides purification catalyst bed which was made to support the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occluded substance and an oxidation catalyst in the fiber layer of the downstream of said filter, or supported this nitrogen-oxides occlusion reduction type catalyst is carried out, and it is constituted.

[0019] There is a filter which purifies exhaust gas among this fiber laminating type of the filters one layer thru/ or by forming several layers in piles, pinching the layered product of this fiber layer at a heat-resistant wire gauze, bending in the shape of bellows, constituting in a bell shape, and circulating exhaust gas from an outside to the inside about the fiber layer of the nonwoven fabric which carried out the laminating of the fiber metallurgy group fiber of ceramics, such as an alumina, at random.

[0020] The dipping of the fiber layer of a besides style side or the downstream is carried out to the solution of each catalyst, and the fiber front face which forms a fiber layer is made to support each catalyst, and it forms in it. Or the porous catalyst coat layer which applied to the front face of the fiber layer of the upstream of the layered product of the fiber layer of a fiber laminating type filter the porous catalyst coat layer which supported the oxidation catalyst, and supported the same NOx occlusion reduction type catalyst as the above on the front face of the fiber layer of the downstream is applied.

[0021] By these configurations, an oxidation catalyst into the upstream part of a filter moreover, by making the downstream support an NOx occlusion reduction type catalyst, respectively Since oxidize the sulfur oxide (SOx) in exhaust gas by the oxidation catalyst of the upstream, and it is made to combine with calcium, Zn, Fe, etc. in exhaust gas, is made solid sulfate and uptake is carried out to a filter. The attainment to the NOx occlusion reduction type catalyst of SOx can be prevented, and sulfur poisoning of an NOx occlusion reduction type catalyst can be avoided.

[0022] And although NOx occlusion capacity will decline if CO exists in exhaust gas when an air-fuel ratio is Lean's NOx occlusion operation since the NOx occlusion reduction type catalyst has the property which emits a nitrogen dioxide (NO2) from an NOx occluded substance, if a carbon monoxide (CO) exists in the exhaust gas purge of this invention, since it oxidizes and CO in exhaust gas is removed by the oxidation catalyst of the upstream, an air-fuel ratio can maintain highly the NOx occlusion capacity at the time of Lean.

[0023] Moreover, since a lot of CO occurs in order that there may be no oxygen (O2) into exhaust gas when it is playback operation with a rich air-fuel ratio, this CO is NO2 from an NOx occluded substance. It is NO2 emitted since this CO becomes a reducing agent while promoting emission. Reduction purification is efficiently carried out by the oxidation catalyst of an NOx occlusion reduction type catalyst.

[0024]

[Embodiment of the Invention] Hereafter, the exhaust gas purge of the gestalt of operation concerning this invention is explained, referring to a drawing.

[0025] The configuration of the exhaust gas purge 1 of the gestalt of this 1st operation is shown in drawing 1.

[0025] As shown in drawing 1, this exhaust gas purge 1 is equipment formed in the flueway 3 of a diesel power plant 2, is equipped with the filter 4 of the Wall flow type which purifies the particulate matter (PM) and nitrogen oxides (NOx) in exhaust gas G, and is constituted.

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of PM combustion at the time of filter playback was lessened, and degradation of an NOx reduction catalyst is prevented.

[0008]

[Problem(s) to be Solved by the Invention] However, in these exhaust emission control devices proposed by JP.2000-282852.A, since the NOx reduction catalyst is used for NOx purification, it is necessary to always supply reducing agents, such as a hydrocarbon, for NOx reduction, and the reducing-agent feeder for supplying this reducing agent is needed.

[0009] And when an engine fuel is diverted to this reducing agent in the injection valve and piping for injecting a fuel to a flueway are needed upwards, and there is a problem of causing aggravation of fuel consumption and using ammonia and the ureas other than an engine fuel. There is a problem that in addition to an injection valve or piping the tank for these reducing agents is needed upwards, and it is necessary to supply these reducing agents to the tank for reducing agents suitably.

[0010] If installation of the reducing-agent distribution system to this flueway is needed, since the activity at the time of attaching exhaust gas equipment in the existing car will become troublesome especially, the problem that become the field of an activity man day to a cost rise also from an equipment side, and utilization becomes difficult occurs.

[0011] Moreover, since the oxidation catalyst is arranged at the upstream of the NOx reduction catalyst which needs a reducing agent especially, When a reducing agent is gas oil, although it is decomposed by the oxidation catalyst, and it becomes the hydrocarbon of low molecular weight with sufficient NOx reduction effectiveness, and SOF (fusibility organic component) is also decomposed and NOx is efficiently returned as a reducing agent. Like the usual combustion condition of a diesel power plant, when the oxygen density under exhaust air is high, possibility that the reducing agent supplied in the flueway will oxidize according to the oxidation catalyst of the upstream is large, and NOx reduction effectiveness also falls and is considered to cause aggravation of fuel consumption.

[0012] On the other hand, an NOx occlusion reduction type catalyst is in one of the catalysts for removing NOx in exhaust gas. This NOx occlusion reduction type catalyst is a catalyst which supports NOx occluded substances, such as barium with an NOx occlusion function, and activity catalyst metals (oxidation catalyst), such as platinum which has an oxidation catalyst function, and achieves the function of NOx occlusion, NOx emission, and reduction purification by the oxygen density in exhaust gas etc.

[0013] Made in order that this invention may solve an above-mentioned problem, arranging an oxidation catalyst into the upstream part of the filter of DPF, and it arranging an NOx occlusion reduction type catalyst into a downstream part, respectively, and avoiding sulfur poisoning which is the weak spot of an NOx occlusion reduction type catalyst, the purpose is a high rate of NOx purification, and is to offer the exhaust gas purge which can purify PM and NOx in exhaust gas.

[0014]

[Means for Solving the Problem] The exhaust gas purge for attaining the above purposes is constituted as follows.

[0015] 1) While being prepared in an engine flueway and preparing the oxidation catalyst layer which supported the oxidation catalyst into the upstream part of the porosity wall surface of said filter in the exhaust gas purge equipped with the filter of the Wall flow type which purifies the particulate matter in exhaust gas, the nitrogen-oxides purification catalyst bed which supported the nitrogen-oxides occlusion reduction type catalyst which includes a nitrogen-oxides occluded substance and an oxidation catalyst in the downstream part of the porosity wall surface of said filter is prepared, and it is constituted.

[0016] This Wall flow type of filter can be formed by the monolith honeycomb which *****ed) the porous inlet port and porous outlet of a channel of a ceramic by turns, and the oxidation catalyst layer which supported the oxidation catalyst can be formed in porous catalyst coat layers applied to the porosity wall surface of this filter, such as a zeolite and an alumina, by carrying out supporting the oxidation catalyst of platinum (Pt), cerium oxide (CeO2), etc. [of a honeycomb]

[0017] Moreover, a nitrogen-oxides (NOx) occlusion reduction type catalyst O2 in exhaust gas

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JP.2003-001067.A [DETAILED DESCRIPTION]

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[0027] As shown in drawing 2, this Wall flow type of filter 4 has the channel (cel) 35 of many polygon configurations used as the path of exhaust gas G in the support 30 of the structure material formed by cordierite, silicon carbide (SiC), stainless steel, etc., and is formed by the monolith honeycomb which *****ed) the porous inlet port and porous outlet of a channel 35 of a ceramic by turns. [of a honeycomb]

[0028] And as shown in drawing 3 and drawing 4, while forming the oxidation catalyst layer 20 which supported the oxidation catalyst 21 and in which aeration is possible in upstream partial 30u of the porosity wall surface 30 of this filter 4, the NOx purification catalyst bed 40 which supported the nitrogen-oxides occlusion reduction type catalyst (NOx occlusion reduction type catalyst) 41 which contains nitrogen-oxides occluded substance (NOx occluded substance) 41a and oxidation catalyst 41b in 30d of downstream parts of the porosity wall surface 30 of a filter 4 and in which aeration is possible is formed.

[0029] This oxidation catalyst layer 20 supports ***** 21, such as platinum (Pt) etc., and cerium oxide (CeO2), in porous catalyst coat layers applied to upstream partial 30u of the porosity wall surface 30 of this filter 4, such as a zeolite and an alumina (aluminum 2O3), and is formed in them possible [aeration].

[0030] Moreover, the NOx purification catalyst bed 40 supports the NOx occlusion reduction type catalyst 41 which becomes porous catalyst coat layers applied to 30d of downstream parts of the porosity wall surface 30 of a filter 2, such as a zeolite and an alumina, from NOx occluded substance 41a and oxidation catalyst 41b, and is formed.

[0031] The potassium in which this NOx occluded substance 41a has an NOx occlusion function (K), Alkali metal, such as barium (Ba), sodium (Na), a lithium (Li), and caesium (Cs). It is formed in one or some combination in rare earth, such as alkaline earths, such as calcium (calcium), a lanthanum (La), and an yttrium (Y), etc., and oxidation catalyst 41b is formed with catalytic activity metals, such as platinum (Pt) and a rhodium (Rh).

[0032] By this configuration, the NOx occlusion reduction type catalyst 41 As typically shown in drawing 9, when the air-fuel ratio in exhaust gas is in the Lean condition (O2 concentration is comparatively high), occlusion of NOx is carried out by NOx occluded substance 41b. When an air-fuel ratio is in a rich condition (O2 concentration is almost zero), NOx will be emitted by NOx occluded substance 41b, and it will have the function which returns with reducing agents, such as CO and HC, by the catalysis of oxidation catalyst 41b, and purifies this emitted NOx.

[0033] Next, exhaust gas purge 1A of the gestalt of the 2nd operation is explained.

[0034] The types of the filter with which exhaust gas purge 1A of the gestalt of this 2nd operation purifies the exhaust gas purge 1 of the gestalt of the 1st operation and the particulate matter in exhaust gas (PM) as shown in drawing 5 - drawing 7 differ.

[0035] The filters 4A, 4B, and 4C of the gestalt of this 2nd operation As shown in drawing 5 - drawing 10, it is formed with a fiber laminating type filter. Or several layers are formed in piles. The fiber layers 5a-5d of the nonwoven fabric which carried out the laminating of the fiber metallurgy group fiber of ceramics, such as an alumina, at random — one layer — The these fiber layers [5a-5d] layered products 5A, 5B, and 5C are pinched at the heat-resistant wire gauzes 6 and 7, and it bends in the shape of bellows, and constitutes in a bell shape, and end side 4a of this hollow cylinder is blocked. From the outside of the these bell shape fiber layers [5a-5d] layered products 5A, 5B, and 5C, exhaust gas G circulates to the inside, is purified inside, and is discharged from other end side of centum 4b outside.

[0036] And as shown in drawing 8 and drawing 9, the porous catalyst coat layer 40 which applied to the front face of fiber layer 5a of the upstream of these filters 4A and 4B the porous catalyst coat layer 20 which supported the oxidation catalyst 21, and supported the NOx occlusion reduction type catalyst 41 on the front face of 5d of fiber layers of the downstream is applied. Drawing 8 shows the example of layered product 5A which formed the porous catalyst coat layers 20 and 40 in the heat-resistant heat-resistant wire gauze [of fiber layer 5a] 6, and wire gauze 7 side of 5d of fiber layers, and drawing 9 shows the example of layered product 5B which formed the porous catalyst coat layers 20 and 40 between fiber layer 5a and fiber layer 5b and between 5d of fiber layers, and fiber layer 5c.

[0037] Or after carrying out the dipping of the fiber layers 5a and 5d of the upstream or the

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downstream to the solution of each catalyst 31 and 41 and making the fiber front face which dries and heat-treats and forms the fiber layers 5a and 5d support each catalyst 31 and 41. As shown in drawing 10, a laminating is carried out to fiber layer 5a' which supported these catalysts 31 and 41, and the fiber layers 5b and 5c which are not supporting the catalyst for 5d', and layered product 5C is formed. In addition, the fiber layer 5 which constitutes filter 4C — the fiber layer which all boils a-5d, is made to support one of catalysts, and is not supporting the catalyst may be excluded and formed.

[0038] Since according to the exhaust gas purges 1 and 1A of the above configuration it is discharged after exhaust gas G contacts an oxidation catalyst 21, passes Filters 4, 4A-4C to other backward one and contacts it further at the NOx occlusion reduction type catalyst 41, it is efficiently purified in the following processes.

[0039] First, it is O₂ in exhaust gas like usual operations, such as a usual diesel power plant, a usual lean combustion gasoline engine, etc. The air-fuel ratio contained in the condition that Lean's oxygen density is comparatively high. As shown in drawing 11, by oxidation catalyst 41b of the oxidation catalyst 21 of the upstream of Filters 4, 4A-4C, or the NOx occlusion reduction type catalyst of the downstream NO in exhaust gas G O₂ in this exhaust gas G it oxidizes and is NO₂. It becomes and is this NO₂. Since NOx occluded substance 41a, such as barium (Ba), carries out occlusion in the form of a nitrate (for example, Ba₂(NO₃)₂) etc., NOx in exhaust gas G is purified.

[0040] Moreover, by the oxidation catalyst 21 of the upstream, oxidation purification of HC in exhaust gas G and CO is carried out, and degradation of the NOx occlusion capacity by CO of the NOx occlusion reduction type catalyst 41 is prevented. Moreover, uptake of the PM, such as SOOT (soot: soot), is carried out by the layered products 5A-5C of the porosity wall surface 30 of Filters 4, 4A-4C, or fiber.

[0041] If this condition continues, however, NOx occluded substance 41a with an NOx occlusion function. Since it changes to a nitrate etc. altogether and an NOx occlusion function is lost, engine operational status is changed. The rich combustion which is an air-fuel ratio near theoretical air fuel ratio and theoretical air fuel ratio. A short time O₂ in exhaust gas which performs for (for example, about 0.1 seconds — about 5 seconds), and is called rich spike gas. The hot exhaust gas made into abbreviation zero is generated, and it sends and regenerates for the NOx occlusion reduction type catalyst 41.

[0042] Most oxygen densities with the rich air-fuel ratio which reproduces the NOx occlusion reduction type catalyst 41 and in a zero state. At the upstream of Filters 4, 4A-4C, it is O₂. Since there is almost nothing, HC and CO pass to the downstream, without oxidizing, and at the downstream, it is O₂. Since there is almost nothing. The nitrate (barium nitrate) of NOx occluded substance 41a which carried out occlusion of NOx as shown in drawing 12 etc., is return and NO₂ which was carrying out occlusion to the original condition (barium). It emits.

[0043] Since there is much CO at the time of this playback, it is NO₂ from NOx occluded substance 41a. Since emission and reduction purification can be promoted, the time amount which playback of NOx occlusion capacity takes can be shortened.

[0044] This emitted NO₂ the inside of exhaust gas — O₂, CO, HC, and H₂ in the exhaust gas which has passed the layered products 5A-5C of the porosity wall surface 30 or fiber by the catalysis of oxidation catalyst 41b since it does not exist etc. — a reducing agent — carrying out — nitrogen N₂ it is returned and purifies — having — H₂O and CO₂. It is discharged. Moreover, uptake of the PM, such as SOOT, is carried out by the layered products 5A-5C of the porosity wall surface 30 or fiber.

[0045] And since it oxidizes by the oxidation catalyst 31 of the upstream, and the sulfur oxide (SO_x) in exhaust gas is combined with calcium, Zn, Fe, etc. in exhaust gas, and can be made into solid sulfate and this sulfate can carry out uptake of it in the layered products 5A-5C of the porosity wall surface 30 or fiber, the contact to the NOx occlusion reduction type catalyst 41 of SO_x is prevented, and sulfur poisoning of the NOx occlusion reduction type catalyst 41 can be avoided.

[0046]

[Effect of the Invention] According to the exhaust gas purge of this invention, the following

effectiveness can be done so as explained above.

[0047] Without always supplying the reducing agent for NOx reduction, with the filter which supported the oxidation catalyst and the NOx occlusion reduction type catalyst, by uptake, the occlusion according NOx to an NOx occlusion reduction type catalyst, and the emission and reduction in exhaust gas, while being able to oxidize and purify, since PM in exhaust gas can be purified efficiently, a reducing-agent feeder becomes unnecessary about it, and aggravation of fuel consumption can be prevented.

[0048] An oxidation catalyst into the upstream part of a filter and by moreover, the configuration which arranges an NOx occlusion reduction type catalyst in a downstream part. Since oxidize the sulfur oxide (SO_x) in exhaust gas by the oxidation catalyst of an upstream part, it is made to combine with calcium, Zn, Fe, etc. in exhaust gas, it considers as the sulfate of the solid-state which can carry out uptake with a filter and uptake is carried out with a filter. SO_x in exhaust gas can prevent reaching to an NOx occlusion reduction type catalyst, and can avoid sulfur poisoning of an NOx occlusion reduction type catalyst.

[0049] Furthermore, since an air-fuel ratio carries out oxidation removal of CO in exhaust gas by the oxidation catalyst of the upstream of a filter in Lean's NOx occlusion operation. Degradation of the NOx occlusion capacity by CO is prevented, and the high rate of purification can be maintained, and it sets to playback operation with a rich air-fuel ratio, and is O₂ in exhaust gas. By CO generated in order for there to be nothing NO₂ from an NOx occluded substance. Emission and reduction purification can be promoted and the time amount which playback of NOx occlusion capacity takes can be shortened.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing arrangement of the exhaust gas purge concerning this invention.

[Drawing 2] It is drawing concerning this invention showing the configuration of the 1st Wall flow type filter of the exhaust gas purge of the gestalt of operation.

[Drawing 3] It is the enlarged drawing of the filter of drawing 2.

[Drawing 4] It is the partial enlarged drawing of the filter of drawing 2.

[Drawing 5] It is drawing concerning this invention showing the configuration of the 2nd fiber laminating type filter of the exhaust gas purge of the gestalt of operation.

[Drawing 6] It is drawing showing the flow of the exhaust gas in the filter of drawing 5.

[Drawing 7] It is the partial enlarged drawing of drawing 6.

[Drawing 8] It is drawing showing the 1st example of the laminated structure of the filter of drawing 5.

[Drawing 9] It is drawing showing the 2nd example of the laminated structure of the filter of drawing 5.

[Drawing 10] It is drawing showing the 3rd example of the laminated structure of the filter of drawing 5.

[Drawing 11] Typical drawing showing the mechanism of the NOx purification by the NOx occlusion reduction type catalyst shows the condition that air-fuel ratios, such as combustion, usually supply the exhaust gas of the Lean condition.

[Drawing 12] Typical drawing showing the mechanism of the NOx exhaust air purification by the NOx occlusion reduction type catalyst shows the condition that the air-fuel ratio supplies the exhaust gas of a rich condition.

[Description of Notations]

1, 1A, 1B, 1C Exhaust gas purge

2 Engine

3 Flueway

4 Wall Flow Type Filter

4A, 4B, 4C Fiber laminating type filter

4a The fiber layer of the upstream

4d Fiber layer of the downstream

20 Oxidation Catalyst Layer (Porous Catalyst Coat Layer)

21 Oxidation Catalyst

30 Porosity Wall Surface

40 Nitrogen-Oxides Purification Catalyst Bed (Porous Catalyst Coat Layer)

41 Nitrogen-Oxides Occlusion Reduction Type Catalyst (NOx Occlusion Reduction Type Catalyst)

41a Nitrogen-oxides occluded substance (NOx occluded substance)

41b Oxidation catalyst

G Exhaust gas

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